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*[Note: Very poor copy of the original. Names, addresses, company names and brand names are translated in the most common manner. Japanese language does not have singular or plural words unless otherwise specified by a numeral prefix or a general form of plurality suffix.]*

**Description of the Invention****1. Name of the Invention****Manufacturing Method for High Melt Point Glass Body****2. Scope of the Claims**

Manufacturing method for the preparation of high melt point glass body characterized by the fact that a sintered body from a mixed material that is an Al<sub>2</sub>O<sub>3</sub> – Ln<sub>2</sub>O<sub>3</sub> system (where Ln represents rare earth metal element and yttrium element), which is difficult to form a glass state, and which is formed as relative to the fine powder material of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, one type or two or more types of any Ln<sub>2</sub>O<sub>3</sub> fine powder materials, are added, is heated at a temperature of approximately 2500°C or higher, and preferably at a temperature of 3000°C or higher using an arc plasma flame, and it is melted, and this is then rapidly cooled and a transparent to visible light beam ceramics glass body is obtained continuously.

**3. Detailed Description of the Invention**

The present invention is an invention about a large scale manufacturing method where a high melting point oxide material, which is difficult to form a glass state, and its system, are melted by using an arc plasma flame and this material is supplied in the gap between cooling rolls that are rotating at a high speed, and it is rapidly cooled and it becomes a material in a glass state, and a ceramic glass body that is transparent to visible light is obtained.

Among the many oxide compounds, as it is well known, as the components that easily form a glass state there are B<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, GeO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, As<sub>2</sub>O<sub>5</sub>, etc. The present invention is an invention whereby relative to this, improves the rapid cooling methods used according to the previous technology relative to the oxide compounds and their systems, which are difficult to form a glass state, like for example, Al<sub>2</sub>O<sub>3</sub> – Ln<sub>2</sub>O<sub>3</sub> (where Ln represents rare earth metal element and yttrium element), and it uses an arc plasma flame and an impact quenching etc., high speed cooling method, and it realizes a new Al-Ln-O glass state.

Namely, it is an invention that suggests a manufacturing method for the preparation of a glass body from an Al<sub>2</sub>O<sub>3</sub> – Ln<sub>2</sub>O<sub>3</sub> system (where Ln represents rare earth metal

element and yttrium element), which has been said to be difficult to form a glass state according to the previous technology, and according to the present invention, first a sintered body which is formed as relative to the fine powder material of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, one type or two or more types of any Ln<sub>2</sub>O<sub>3</sub> fine powder materials, are added, is heated at a temperature of approximately 2500°C or higher, and preferably at a temperature of 3000°C or higher using an arc plasma flame, and it is melted, and this is then rapidly cooled, for example by the method where it is supplied in the gap between cooling rolls rotating at a high speed, and a transparent to visible light beam ceramics glass body is obtained continuously.

Here below, an explanation will be provided relative to the manufacturing of Al<sub>2</sub>O<sub>3</sub> – Ln<sub>2</sub>O<sub>3</sub> system glass body.

Granulated below 325 mesh (45 microns), fine powder form, high melting point oxides of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Ln<sub>2</sub>O<sub>3</sub> were mixed at different mole ratios, and sintered bodies with a cylindrical shape with dimensions of 3 mm diameter x 30 mm, were formed. This sintered bodies were placed in a chuck and their edges were melted by a two stand arc plasma flame and the molten material flowed in the gap between two rotating at a high speed rollers of an inner part cooling device and by that it was possible to produce a transparent to the visible light experimental material with a thickness of approximately 1 micron and a diameter of approximately 50 mm. Regarding the mole ratio of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and the Ln<sub>2</sub>O<sub>3</sub> in this case, it is preferred that the ratio of the Ln<sub>2</sub>O<sub>3</sub> relative to 1 mole of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> be within the range of 0.1 – 10 moles. Naturally, when both materials are used individually a glass body is not obtained. The fact whether or not the obtained by this method experimental material is a glass material was studied by using a polarized light microscope, an X-Ray diffraction and an electron microscope. According to the method using a polarized light microscope, the experimental material was placed in the space between orthogonal Nicol and an orthoscopic observation was conducted. For the experimental material, even if the stage was rotated, a change in the image contrast was not observed. Then, for the X-ray diffraction image and for the electron beam diffraction image, only a halo image was observed. In the viewing field by the electron microscope there was no intervening material observed. In Figure 1 the electron beam diffraction image (Figure 1 – 1) of the experimental material from the Al-Ln-O system and its planar viewing field image (Figure 1 – 2), are presented. The phenomenon of crystallization of the Al-Ln-O system experimental material by subjecting it to a thermal treatment at a temperature of 1000°C for different number of hours was studied by using X-ray diffraction. The results from that are shown in Figure 2. From the above-described observations it is possible to determine that the experimental material obtained by using the above-described equipment is a glass material. Regarding such glass material, it is possible to obtain various compositions of the Al-Ln-O system, and the elements that are represented by the above described Ln are La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y. Regarding the produced glass material, it is transparent relative to visible light, and also, regarding the Ln element, usually, the elements that are present in a third valency are stable, however, among the Al-Ln-O glass materials, the materials where Ln is Sm, Eu and Yb and these elements are present in a bivalent state, it is

considered that a coloration is developed. In Figure 3 the obtained glass material is presented.

The coloration of the obtained Ln-Al-O system glass is according to the described here below.

<u>Ln-Al-O</u>	<u>Color</u>
La-Al-O	colorless
Ce-Al-O	colorless
Pr-Al-O	pale green color
Nd-Al-O	pale blue color
Sm-Al-O	brown color
Eu-Al-O	pale yellow color
Gd-Al-O	colorless
Tb-Al-O	colorless
Dy-Al-O	colorless
Ho-Al-O	colorless
Er-Al-O	pale orange color
Tm-Al-O	colorless
Yb-Al-O	pale brown color
Lu-Al-O	colorless
Y-Al-O	colorless

Regarding the glass materials that is obtained by using the above described glass material manufacturing installation, and using an oxide material or its system that are difficult to form a glass state irrespective of the type of the used Al-Ln-O system, it is anticipated that they are materials that have properties that are different from those of the glass materials obtained according to the previous technology from glass, B<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, etc., and it is considered that from the standpoint of the optical, electric and magnetic properties, they are materials that can play an extremely important role in the different aspects of the electronic memory related technologies and also in other processing technologies.

### Practical Examples

The manufacturing of high melting point ceramic glass materials uses the equipment presented according to Figure 4. Here below an explanation will be provided by using the figure.

In the figure, 1 represents a chuck whereby in order to produce the glass material, the sintered body experimental material can be moved in the up and down direction within the diagram. Also, in the figure, 2 represents the sintered rod. The material used in order to obtain the glass material, is a material where less than 325 mesh dispersity, fine powder form  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Ln<sub>2</sub>O<sub>3</sub>, for example, La<sub>2</sub>O<sub>3</sub>, powder are weighed at the

corresponding mole ratio, and after that these are well mixed and combined by using a mixing device, and this material is press molded in a cylindrical shape with dimensions of 3 mm diameter x 50 mm, and this cylinder shape material is sintered at a temperature of approximately 1000°C for a period of 20 hours in an air atmosphere. The cylinder shaped sintered material body 2 is grasped by the chuck 1 so that, as shown according to the presented in Figure 1, its front end is introduced into an arc plasma flame. 3 represents argon arc plasma flame (with a temperature of at or above approximately 3000°C), and it is at a temperature of approximately 2500°C or above, and preferably, it is at or above approximately 3000°C. 4 represents the arc plasma nozzle, 5 represents the roller where the inner part is cooled by water, and that rotates at 1000 rpm or higher, and where by the motion in the left and right direction, it is possible to adjust the thickness of the glass material. The molten material obtained from the sintered body enters in the gap between the two rollers that are rotating at a speed of approximately 1000 rpm, and from the rollers, a transparent glass material with a thickness of approximately 1 micron, is obtained. The obtained glass material has a diameter in the range of 50 ~ 100 mm. Moreover, the details of the cooling part are shown in Figure 5. 6 (in Figure 4) represents the experimental material controlling device, 7 represents the produced glass material. This glass material is collected in the receptacle tray 8.

In Figure 5, 9 represents the motor used for the rotation, 10 represents the entrance in the cooling part where the cooling part used cooling water is transported, 11 represents its exit opening. The cooling water enters through the above described opening 10 close to the roller inside part separation wall 12 and it cools the roller surface. The water that has a somewhat higher temperature is directed to exit through the exit opening 11 by 13, which is close to the axis part.

Moreover, in Figure 6, a schematic diagram is shown of the essential parts of the device generating the above described argon arc plasma. If we are to provide a simple description, through the protection gas nozzle 14, as a protective gas 15, for example, a mixed gas containing 93 volume % Ar and 7 volume % H<sub>2</sub> is used. 16 represents the melt injection head, 17 represents the cooling water. 18 represents the plasma gas (Ar), 19 represents the a tungsten electrode (- electrode), 20 represents a high frequency wave, 21 represents the electric source for the pilot arc, 23 represents the electric source for the melt injection arc. 23 represents a switch, 24 represents an arc plasma flame, 25 represents a (+electrode).

After that, the glass material that is obtained by using this equipment is presented in Figure 3.

In the case of this glass material, it can obtained from all rare earth type elements and yttrium element (Y) and also, it can obtained from almost all the mole ratios of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Ln<sub>2</sub>O<sub>3</sub>, however, it is preferred that relative to 1 mole of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, the amount of the Ln<sub>2</sub>O<sub>3</sub> is within the range of 0.1 ~ 10 moles. The confirmation of the glass state of the material was conducted by using polarized light microscope, X ray diffraction and electron beam diffraction.

In the above described Figure 1, the electron beam diffraction pattern and the microscopic image of the glass material obtained as  $\text{Al}_2\text{O}_3$ :  $\text{Ln}_2\text{O}_3 = 6:1$  are weighed, as a representative example of the Al-Ln-O system, are shown. For the electron microscope a manufactured by Nippon Denko Company, 200 kV microscope, was used. Regarding the electron beam diffraction image, it was projected at an acceleration electric potential of 150 kV, and it showed a typical halo image. The fact that this halo image was obtained indicates that the obtained experimental material is a glass material. Regarding the electron microscopic image, it is an image obtained by a bright viewing field image at a magnification of 62,000 times. From this image it is seen that there are no intervening materials present at all and this indicates that the obtained glass material is a microscopically good glass material. Then, by the observation through a polarized light microscope, it is confirmed that even when the experimental material is rotated, there is no change in the contrast at all, and this indicates that macroscopically also it is a good glass material. Also, in Figure 2, the results are shown from a measurement conducted by an X-ray diffractometer using  $\text{CuK}\alpha$  relative to the manufactured glass material after it has been subjected to a thermal treatment for the time period as shown in the figure, and this studies the conditions of the crystallization.

As it has been described here above, according to the present invention it is possible to suggest a manufacturing method for the preparation of high melt point glass body characterized by the fact that a sintered body from a mixed material that is an  $\text{Al}_2\text{O}_3$  –  $\text{Ln}_2\text{O}_3$  system (where Ln represents rare earth metal element and yttrium element), which is difficult to form a glass state, and which is formed as relative to the fine powder material of  $\alpha$ - $\text{Al}_2\text{O}_3$ , one type or two or more types of any  $\text{Ln}_2\text{O}_3$  fine powder materials, are added, is heated at a temperature of approximately 2500°C or higher, and preferably at a temperature of 3000°C or higher using an arc plasma flame, and it is melted, and this is then rapidly cooled by using for example a method where this molten material is rapidly cooled in the space between rotating at a high speed cooling rollers and a transparent to visible light beam ceramics glass body is obtained continuously.

Here above, mainly, a practical example was described where  $\text{La}_2\text{O}_3$  was used as the  $\text{Ln}_2\text{O}_3$ , and also, as the rapid cooling method for the material that has been melted by the argon arc plasma, water cooled type, high-speed rotating rollers were used, however, after this, as other practical example, there is the example where  $\text{Nd}_2\text{O}_3$  was used as the  $\text{Ln}_2\text{O}_3$ , and where for the rapid cooling method, the equipment shown according to Figure 7, that has a structure formed from a water cooled piston 26 and an anvil 27, was used.

Regarding the  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$  that are used as the material, they are both materials where the purity level is at least 99.9 % or higher, and also, they are materials that are in a fine powder form. The mole ratio of both materials, namely,  $\alpha$ - $\text{Al}_2\text{O}_3$ : $\text{Nd}_2\text{O}_3 = x : 1$ , where x was within the range of 1 and 10. Both materials were well pulverized, mixed and combined, and they were subjected to an elevated pressure of 4 ton/cm<sup>2</sup>, and pellets with a thickness of 1 mm and a diameter of 5 mm, were formed. These pellets were sintered in an air atmosphere at a temperature of 1000°C for a period of 5 hours. The pellets 28 of this sintered experimental material were placed inside a manufactured from

Cu piston, as shown according to Figure 7, and they were melted by the plasma flame 25 until the experimental material formed a spherical shape. While heating by using the plasma flame 25, the water cooled by the cooling water 30 piston 26 and the manufactured from copper anvil 27 are operated by the spring 31 and the electro-magnet (not shown in the figure), and the molten material is enclosed in the space between the two and it is rapidly cooled. Moreover, in this case, the above described plasma flame 25 is discharged from the plasma torch 32.

Regarding the produced glass material, at a diameter of approximately 5 mm and a thickness of approximately 1 micron, it is a material that is transparent to visible light beam. The glass material obtained from the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> : Nd<sub>2</sub>O<sub>3</sub> = 6 : 1 experimental material was subjected to a an orthoscopic observation by the polarized light microscopic method, in the space between orthogonal Nicol, and the same way as in the above described practical example, even if the stage was rotated, there was no change in the image contrast. Then, through the X ray diffraction pattern, and the electron beam diffraction image, only a halo pattern was observed. Then, when using an electron microscope, in the bright viewing field image there were no intervening materials observed. Figure 8 is a diagram presenting the results from the X ray diffraction studies of the crystallization phenomenon in the case when the above described Al-Nd-O system experimental material was annealed at a temperature of 1000°C for different number of hours (CuK $\alpha$  radiation, (using Ni filter), pulse height analysis).

From the above described it is confirmed that the isotropic properties possessing materials that are obtained from the 6 $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Nd<sub>2</sub>O<sub>3</sub> obtained from each of the above described experimental materials, are glass materials.

#### 4. Brief Explanation of the Figures

Figure 1-1 represents the electron beam diffraction pattern (150 kV) of the Al-La-O type glass material; Figure 1-2 represents its bright viewing field pattern (x 62500); Figure 2 represents the results from the measurement of the crystallization of the Al-La-O type glass by the X ray diffraction method. Figure 3 represents a photograph of a thin piece of the Al-Ln-O type glass material. Figure 4 represents the glass material manufacturing equipment according to the first practical example of the present invention. Figure 5 represents a front view diagram where one part of the inner part of the cooling roller 5 from Figure 4, has been cut open. Figure 6 represents a schematic diagram showing the essential parts of the argon arc plasma generating equipment according to the present invention. Figure 7 is a glass manufacturing equipment related to another practical implementation example according to the present invention. Figure 8 is a line chart diagram showing the results from the X ray diffraction measurements of the crystallization of the same Al-Nd-O type glass.

- 1.....chuck for the sintered body of the experimental material,
- 2.....sintered rod, 3.....argon arc plasma flame,
- 4.....arc plasma nozzle, 5.....cooling roller,
- 6.....experimental material controlling device,

7.....synthesized glass material, 8.....glass material  
receptacle tray, 9.....motor, 10.....cooling water entrance  
opening, 11.....cooling water exit opening,  
12.....inner part perimeter vicinity, 13.....inner part  
axis vicinity, 14.....protective gas nozzle,  
15.....protective gas, 16.....discharge  
head, 17.....cooling water, 18.....plasma gas (Ar),  
19.....tungsten electrode (- electrode), 20.....high  
frequency, 21.....electric source for the pilot arc,  
22.....electric source for the melt radiation arc,  
23.....switch, 24.....arc plasma flame,  
25.....roller (+ electrode), 26.....piston,  
27.....anvil, 28.....pellets, 29.....plasma flame,  
30.....cooling water, 31.....spring,  
32.....plasma torch.

第1圖-1

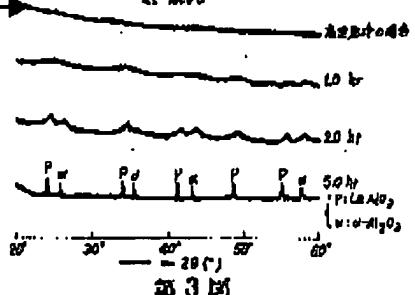


第1圖-2



In the case of high frequency

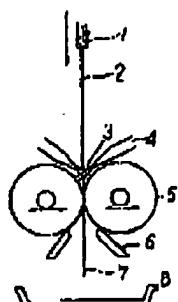
第2図

Al-Li-O ハイドロゲンガス  
at 1000°C

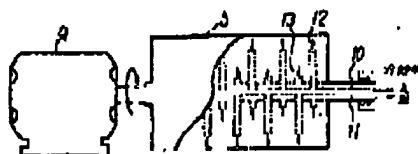
第3図



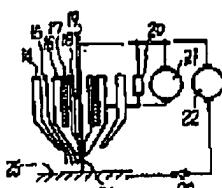
第4図



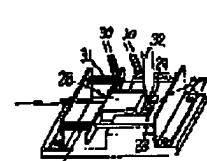
第5図



第6図



第7図



5. 許諾番号の付記

特許	登録	実用	意匠	1. 4
○	○	○	○	○
○	○	○	○	○
○	○	○	○	○

6. 本公報外の開示台、特許出願入または代理人  
山本和也

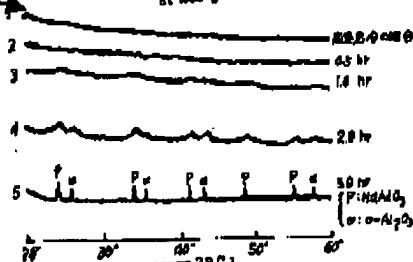
東京高等裁判所大庭町大曾根ノ子安地  
面  
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別  
大

16 上  
99 内  
F  
19  
88

7. 代理人  
山本和也  
東京高等裁判所大庭町大曾根ノ子安地  
面  
分  
別  
大

In the case of high frequency

第8図

Al-Li-O ハイドロゲンガス  
at 1000°C

5. Record of the Appended documents

(1) Description	1 copy
(2) Figures	1 copy
(3) Application copy	1 original
(4) Power of attorney	1 copy

6. Other than the above described invention authors, patent applicants or representatives

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*12/07/04*



急冷せしめる如き高速急冷方法によつて急冷せしめ、可視光線にて透明なセラミックガラス体を得られるようとしたものである。

以下  $Al_2O_3$  -  $Zn_2O_3$  系のガラス体製造に関する説明を行なう。

333 メッシュ (100  $\mu$ ) 以下の大粒度にした銀粉状高融点酸化物  $Al_2O_3$  および  $Zn_2O_3$  を各量のモル比に混合し、3  $\times$  6  $\times$  6  $\times$  6 の円柱状の焼結体にした。この焼結体をテナツで磨きし、その先端を2台のアーチプラズマフレームで溶解し、溶解物を内端面が鏡面のついた高速回転している2台のローターの間に置しとむことによつて約1/8の厚さを有し直径約6mmの可視光線に対して透明な試料を作成することができた。この組合の $Al_2O_3$  と  $Zn_2O_3$  とのモル比は、 $Al_2O_3$  /モルに対し  $Zn_2O_3$  0.1 ~ 10モルが好適である。初期両者の純度の意味ではガラス体は得られていない。このようにして得られた試料がガラス体であるかどうかは偏光顕微鏡、X線回折及び電子顕微鏡によつて調べた。偏光顕微鏡を用いる方法では直交

ニコル間に試料を置き、オルソスコープ観察を行なつた。試料のかいてあるステージを回転しても鏡のコントラストは変化は観察されなかつた。さらには銀回折像、電子顕微鏡像ではヘロ一像しか観察できなかつた。電子顕微鏡による明視野像では介在物は観察されなかつた。次に組合  $Al_2O_3$  系における試料の電子顕微鏡像 (図1-1) 及びその回折像 (図1-2) を示す。 $Al_2O_3$  系の試料を1000°Cでいろいろな時間熱処理するととよつて結晶化する現象をX線回折で調べた。その結果を図2-1に示す。以上の結果より上記の装置で得られた試料はガラス体であることが同定された。このようなガラス体は  $Al_2O_3$  系のあらゆる組成のところで得られ、前記如で示す元素は  $Al$  ,  $Si$  ,  $Pr$  ,  $Yt$  ,  $Th$  ,  $Sm$  ,  $Eu$  ,  $Ca$  ,  $Tb$  ,  $Dy$  ,  $Ho$  ,  $Er$  ,  $Tm$  ,  $Tb$  ,  $Lu$  及び  $Y$  である。作成したガラス体は可視光線に対して透明であり、又この元素は一般には2種で存在するのが確定であるが  $Al_2O_3$  系ガラス体の中では  $Al$  が  $Si$  ,  $Eu$  ,  $Y$  ではそれらの元素が2種で存在している。

と思われる色調を呈している。第1圖に得られたガラス体を示す。

得られた  $Al_2O_3$  -  $Zn_2O_3$  系の透明なガラスの色調は次の如くであつた。

$Zn_2O_3$	色
$Al_2O_3$	無色
$0.0$ - $Al_2O_3$	無色
$Pr$ - $Al_2O_3$	薄い緑色
$Yt$ - $Al_2O_3$	薄い青色
$Th$ - $Al_2O_3$	褐色
$Sm$ - $Al_2O_3$	淡黄色
$Eu$ - $Al_2O_3$	緑色
$Ca$ - $Al_2O_3$	無色
$Tb$ - $Al_2O_3$	無色
$Dy$ - $Al_2O_3$	無色
$Ho$ - $Al_2O_3$	無色
$Er$ - $Al_2O_3$	薄い緑色
$Tm$ - $Al_2O_3$	無色
$Tb$ - $Al_2O_3$	薄い褐色
$Lu$ - $Al_2O_3$	無色
$Y$ - $Al_2O_3$	無色

上記のガラス体製造装置を使用して  $Al_2O_3$  系のみならずガラス状態になり難い酸化物及びその系において得られるガラス体は深緑のガラス、 $B_2O_3$  ,  $SiO_2$  等の系よりなるガラスとは異なつた性質を持つことが予想され、光学的、電気的、磁気的性質の立場から配位電子網体其の他工芸的に各方面で非常に役立つものと思われる。

#### 実験例

本説明セラミックスのガラス体焼成は第1圖に示す装置を使用する。以下図面を用いて説明を行なう。

1はガラス体を作成する為の焼結体試料チャックで焼成中で上下に動作できる。2は焼結体を示す。ガラス体を得る為の試料は、333メッシュ以下の大粒度にした銀粉状 $Al_2O_3$  と  $Zn_2O_3$  例えば  $Zn_2O_3$  の粉末を適当なモル比に秤量した後、搅拌器でよく混合した後6  $\times$  6  $\times$  6の円柱状にプレス成形した。この円柱状物を約1000°Cで2時間大気中で焼成したものである。円柱状焼結体2を図1-1に示すようなテナツノに接着し、先端がアルゴンア

・クラスマフレームの中に入るよう設置する。これはアルゴンアーキプラズマフレーム（約3000℃以上の温度）を示し、約2800℃以上、好ましくは約2000℃以上である。アーキアーキクラスマノズルを示す。これは水で内冷却してあるローターを示し、1000 rpm以上で回転し、左方に移動するとよつてガラス体の厚さを調節できる。鏡面体が導入した面積約1000 mm<sup>2</sup>の面で回転している2台のローターの間に入りローターからは約1/2の厚さを持つ透明なガラス体が得られた。得られたガラス体は直角約90°～100°の大きさを有している。

また、冷却部の詳細については図5に示す。これは試料のかきとり盤を示す。これは作成したガラス体を示す。これをガラス体の反対側によつて受けれる。

図5の9は冷却扇動用モーターを示し、10は冷却部分に冷却装置で冷却水を送る入口、11はその出口を示す。冷却水は冷却入口10から入りローター内部の周囲近くに入りロール表面を冷却

する。若干温度の上つた水を冷却の近く12から出口11へ出す。

なお、図6は前記のアルゴンアーキプラズマ発生装置の実際の模式図を示す。標準化試験すると、1は保護ガスノズルで、保護ガスなどとしては、例えば、Ar 99.999モル%、N<sub>2</sub> 0.001モル%の混合ガスを使用する。16は導射ヘッドであり、17はその冷却水である。18はアーチガス（Ar）、19はタンクステン電極（一対数）、20は高周波、21がバイロットアーキのための電源、22が冷却アーキのための電源を示す。23はスイッチ、24はアーキクラスマフレーム、25はローター（+電極）を示す。

次にこの装置を用いて得られたガラス体が図6に示してある。

このガラス体は純土鉱元素のすべておよびイオトリウム元素（I）で構成され、またAl<sub>2</sub>O<sub>3</sub>とZn<sub>2</sub>O<sub>3</sub>の組合せすべてモル比のところで構成され、好ましくはAl<sub>2</sub>O<sub>3</sub> /モル比に対しZn<sub>2</sub>O<sub>3</sub> 0.1～10モルである。ガラス体であることとの同定は偏光顕微鏡、X線回折、電子線回折によつて行なつた。

図5の14にはAl-Zn-O系の典型的な例としてAl<sub>2</sub>O<sub>3</sub> : Zn<sub>2</sub>O<sub>3</sub> = 6 : 1で構成して得られたガラス体の電子線回折像およびX線回折像が示してある。使用した電子回折像は日本電子社製の300 kVのものである。電子線回折像は加速電圧180 kVで撮影し、典型的なハロー像を示している。このハロー像から得られた試料がガラス体であることを示している。電子線回折像は明視野像で63,500倍のものである。この像からこのガラス体には全く介在物が存在せず従前の成績のガラス体であることを示している。さらに偏光顕微鏡による観察で試料を回転してもコントラストの変化が全くないことから本構成でも成績のガラス体であることを示している。また、図5には、導入したガラス体を図に示すよう透明化した後、100 kVの電子線による高解像度電子線回折像によつて構成した結果であり、納品化の様子を調べたものである。

以上述べたように、本発明によれば、ガラス体はなりににくいAl<sub>2</sub>O<sub>3</sub>-Zn<sub>2</sub>O<sub>3</sub>系（但しIは純土鉱元素およびイオトリウム元素（I）を示す）の

高融点酸化物において液相状Al<sub>2</sub>O<sub>3</sub>に対しZn<sub>2</sub>O<sub>3</sub>の間れか、も又はより以上から成る酸化物を加えて成る組合せの鏡面体をアーキクラスマフレームにて約2500℃以上好ましくは約3000℃以上に加熱溶解せしめ、これを高速回転冷却ロール間にて急冷せしめる等の急冷方法を用いるととよつて、可視光線にて透明なセラミックガラス体を構成的に得る高融点セラミックガラス体の製造方法を構成することができる。

以上並としてZn<sub>2</sub>O<sub>3</sub>としてZn<sub>2</sub>O<sub>3</sub>を取り上げ、かつアルゴンアーキプラズマによる構成体の急冷方法として、水冷式高速回転ローラーを採用した実験例について述べたが、次にさらに他の酸化物としてZn<sub>2</sub>O<sub>3</sub>としてBa<sub>2</sub>O<sub>3</sub>を用い、急冷方法として図5に示す如き水冷されたビストン等とかななど（アンビル）から冷却された鏡面を採用した。

料として用いいたAl<sub>2</sub>O<sub>3</sub>およびBa<sub>2</sub>O<sub>3</sub>は共に純度として99.9モル以上のものであり、また冷却水を用いる。両モル比、すなわちAl<sub>2</sub>O<sub>3</sub> :

84,0<sub>3</sub> - x : 1 セメは 1 と 10 の間の範囲にある。内筒をよく粉砕混合し  $100 \text{ g/cm}^3$  に加圧し、厚さ 1 mm 程度のペレットを形成する。このペレットを型枠中にて  $1000^{\circ}\text{C}$  で 1 時間焼結する。この焼結された試料のペレットを図 2 図に示す如きのピストンの中央に置き、試料が球状になるとアラズマフレームがによって精製される。アラズマフレーム 24 によって加熱されながら冷却水および水冷されるピストンおよび鋼製のかなと (アンビル) かとスプリングドリと試験石 (図示せず) で作めさせ、筒筒の間に挟んで溶融試料を急速に冷却させる。なお、この場合前記アラズマフレームがはアラズマトーチ 23 から放出される。

生成したガラス体は直徑約 5 cm、厚さ約 1 cm で可視光線で透明である。 $\text{Al}_2\text{O}_3 : \text{Na}_2\text{O} = 6 : 1$  の試料について得られたガラス体を偏光顕微鏡の方法で直交 24 回転にてオルソスコープ検査を行つた結果、前記実験例におけると同様にステージを回転してもそのコントラストに変化はなかつた。さらにエラスコピック、電子顕微鏡ではハロー像しか

得られなかつた。さらに電子顕微鏡による明視野像では介在物は観察されなかつた。第 2 図は前記の  $\text{Al}-\text{Na}-\text{O}$  系の試料ガラス体を  $1000^{\circ}\text{C}$  で 1 時間アニーリングすることによつて結晶化する現象を X 線回折で調べた結果である (CuK $\alpha$  線 (154 フィルター) 使用、ベルスの高さの分析)。以上の各試験から  $\text{Al}_2\text{O}_3 : \text{Na}_2\text{O} = 6 : 1$  から得られた両方の試料はガラス体であることが同定された。

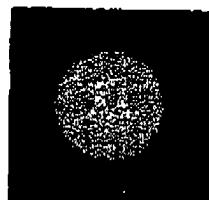
#### 各断面の簡単な説明

第 1 図 - 1 は  $\text{Al}-\text{Na}-\text{O}$  系ガラス体の電子顕微鏡像 (150 EV)、第 1 図 - 2 はその明視野像 ( $\times 62500$ )、第 3 図は  $\text{Al}-\text{Na}-\text{O}$  系ガラスの結晶化の X 線回折像による決定結果、第 4 図は  $\text{Al}-\text{Na}-\text{O}$  系ガラスの断片の写真、第 5 図は第 1 図の冷却ローター 23 の内部を一部剥離して示す正円錐、第 6 図は不透明化するアルゴンアーケープラズマ発生装置の断面を示す模式図、第 7 図は本透明の他の実験例に供するガラス体製造装置、第 8 図は同じく  $\text{Al}-\text{Na}-\text{O}$  系ガラスの結晶化の X 線回折法による決定結果。

示す原因である。

1… 佛焰体燃料チヤンタ、2… 佛焰管、3… アルゴンアーケープラズマフレーム、4… アーケータブスマノズル、5… 冷却ローター、6… 試料かきとり筒、7… 熱したガラス体、8… ガラス体受合、9… モーター、10… 冷却水入口、11… 冷却水出口、12… 内部隔膜附近、13… 内部隔膜附近、14… 保護ガスノズル、15… 保護ガス、16… 導射ヘッド、17… 冷却水、18… アラズマガス (AT)、19… タンクガラス容器 (瓶)、20… 密閉瓶、21… バイロントアーティローラーの側面、22… 导射アーティローラーの側面の側面、23… スイッチ、24… アーケータブスマノズル、25… ローター (冷却筒)、26… ピストン、27… かなとこ (アンビル)、28… ペレット、29… アラズマフレーム、30… 冷却水、31… スプリング、32… アラズマトーチ。

第 1 図 - 1

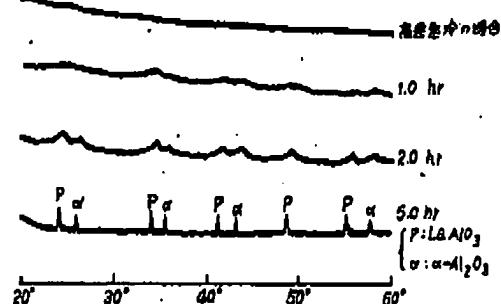


第 1 図 - 2



特開昭50-25608(5)

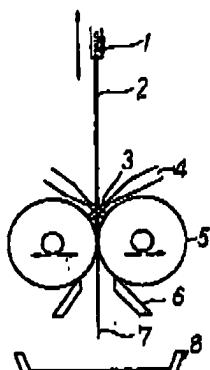
第2図

Al-La-O ハーフエアニアーリング  
at 1000°C

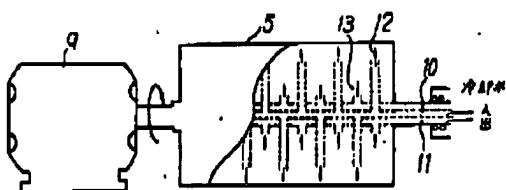
第3図



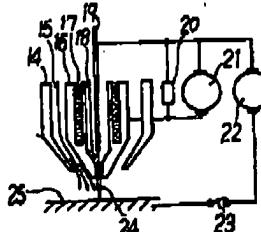
第4図



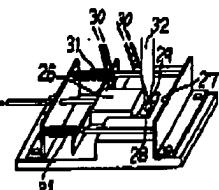
第5図



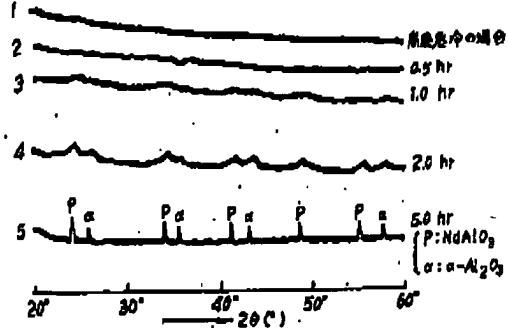
第6図



第7図



第8図

Al-Nd-O ハーフエアニアーリング  
at 1000°C

## 5. 権利要求の目録

(1) 男 品 1 项  
同 上 1 项  
同 上 1 项  
同 上 1 项

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